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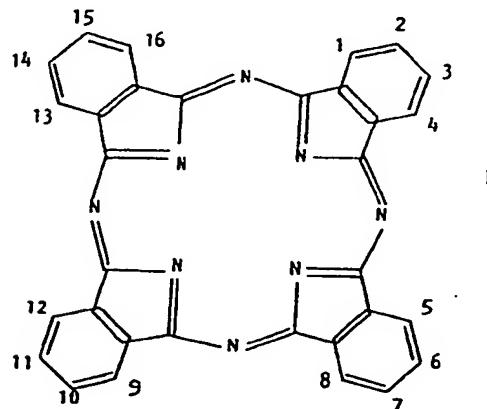
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54 Infra-red absorber.

55 A infra-red absorbing phthalocyanine compound in which each of at least five of the peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 or 16 positions (the "3,6-positions") of the phthalocyanine nucleus, as shown in Formula I, is linked by an atom from Group VB or Group VIB of the Periodic Table, other than oxygen, to a carbon atom of an organic radical. The preferred compounds each of the eight 3,6-positions is linked by an atoms from Group VB or Group VIB, especially sulphur, selenium or nitrogen, to an organic radical.



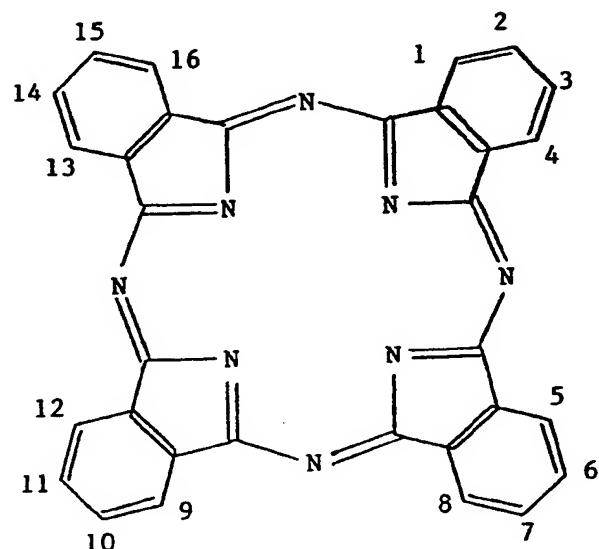
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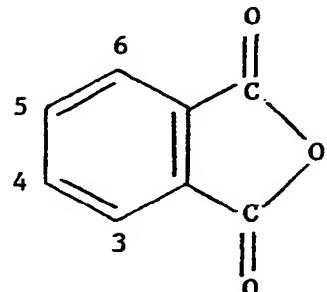
Infra-red Absorber

This specification describes an invention relating to certain poly(substituted)phthalocyanine compounds which absorb in the 5 near infra-red region of the electro-magnetic spectrum, e.g. from 750 to 1500 nm, and more especially from 750 to 1100 nm.

According to the present invention there is provided a phthalocyanine compound in which each of at least five of the 10 peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 or 16 positions of the phthalocyanine nucleus, as shown in Formula I is linked by an 15 atom from Group VB or Group VIB of the Periodic Table, other than oxygen, to a carbon atom of an organic radical.



35 The carbon atoms in the 1, 4, 5, 8, 9, 12, 13, and 16 positions are hereinafter referred to as the "3,6-carbon atoms" by relation to the equivalent 3,6-positions in the four molecules of phthalic anhydride, see Formula II, from which the phthalocyanine can be derived.

5
10

II

The remaining peripheral atoms of the phthalocyanine nucleus
 15 may be unsubstituted, i.e. carry hydrogen atoms, or be substituted by
 other groups, for example, halogen atoms or amino groups, or they may
 also be linked by an atom from Group VB or Group VIB of the Periodic
 Table to a carbon atom of an organic radical. It is preferred that
 each of at least six and, more preferably at least eight, of the
 20 3,6 carbon atoms is linked by a Group VB or Group VIB atom to an
 organic radical.

In a first preferred class of phthalocyanine compound
 according to the present invention each of eight of the peripheral
 carbon atoms, at least five, preferably at least six and more
 preferably all, of which are 3,6 carbon atoms, is linked by an atom
 25 from Group VB or Group VIB to an organic radical. It is further
 preferred that each 3,6 carbon atom is linked to a separate organic
 radical. The remaining peripheral carbon atoms may carry other
 substituents, e.g. halogen atoms, but are preferably unsubstituted.

In a second preferred class each of from nine to sixteen of
 30 the peripheral carbon atoms, at least five, preferably at least six
 and more preferably eight, of which are 3,6 carbon atoms, is linked
 by an atom from Group VB or Group VIB to an organic radical. The
 remaining peripheral carbon atoms are preferably unsubstituted or
 carry halogen atoms. In the second class preferably each of at
 35 least ten, and more preferably at least twelve, of the peripheral
 carbon atoms is linked by a Group VB or Group VIB atom to an organic
 radical. Especially valuable compounds of this second class are
 those in which each of fifteen or sixteen of the peripheral carbon

atoms is linked to an organic radical by an atom from Group VB or Group VIB.

Compounds of especial interest have an absorption peak above 750 nm, especially in the region from 750 to 1100 nm, and those of 5 more especial interest have 90% of their absorption strength at or above 750 nm.

The organic radical may be an optionally substituted aliphatic, alicyclic or aromatic radical and is preferably an optionally substituted aromatic radical, especially from the benzene, 10 naphthalene and mono- or bi-cyclic, heteroaromatic series. Examples of suitable aromatic radicals are optionally substituted phenyl, phenylene, naphthyl, especially naphth-2-yl, naphthylene, pyridyl, thiophenyl, furyl, pyrimidyl and benzthiazolyl. Aliphatic radicals are preferably from the alkyl and alkenyl series containing up to 15 20 carbon atoms, such as vinyl, allyl, butyl, nonyl, dodecyl, octadecyl and octadecenyl. Alicyclic radicals are preferably homocyclic containing from 4 to 8 carbon atoms, such as cyclohexyl. The organic radical may be monovalent and attached to a single peripheral carbon atom through a single Group VB or Group VIB atom or 20 it may be polyvalent, preferably divalent, and attached to adjacent peripheral carbon atoms through identical or different atoms from Group VB and Group VIB. Where the organic radical is polyvalent it may be attached to two or more phthalocyanine nuclei.

Examples of substituents for the aromatic and heteroaromatic 25 radicals are alkyl, alkenyl, alkoxy and alkylthio, and halo substituted derivatives thereof, especially those containing up to 20 carbon atoms, aryl, arylthio, especially phenyl and phenylthio, halogen, nitro, cyano, carboxyl, aralkyl, aryl- or alkyl-sulphonamido, aryl- or alkyl- sulphone, aryl- or 30 alkyl-sulphoxide, hydroxy and primary, secondary or tertiary amino.

Examples of substituents for the aliphatic and cycloaliphatic radicals are alkoxy, alkylthio, halo, cyano and aryl. In these substituents the alkyl and alkenyl groups preferably contain up to 20, and more preferably up to 4, carbon atoms and the aryl groups are

preferably mono- or bi-homo- or hetero-cyclic. Specific examples of substituents are methyl, ethyl, dodecyl, methoxy, ethoxy, methylthio, allyl, trifluoromethyl, bromine, chlorine, fluorine, benzyl, COOH, -COOCH₃, -COOCH₂C₆H₅, -NHSO₂CH₃, -SO₂C₆H₅, NH₂, -NHC₂H₅, and N(CH₃)₂

5 Examples of suitable atoms from Group VB and Group VIB for linking the organic radical to a peripheral carbon atom of the phthalocyanine nucleus are sulphur, selenium, tellurium and nitrogen or any combination of these. Where an organic radical is linked to adjacent peripheral carbon atoms the second bridging atom may be any 10 atoms from Group VB or Group VIB and examples are sulphur, oxygen, selenium, tellurium and nitrogen. Where the linking atom is nitrogen the free valency may be substituted or unsubstituted e.g. it may carry an alkyl group, preferably C₁₋₄-alkyl or an aryl group, preferably phenyl.

15 The phthalocyanine nucleus may be metal free, i.e. it may carry two hydrogen atoms at the centre of the nucleus, or it may be complexed with a metal or oxy-metal derivative, i.e. it may carry one or two metal atoms or oxy-metal groups complexed within the centre of the nucleus. Examples of suitable metals and oxy-metals are copper, 20 lead, cobalt, nickel, iron, zinc, germanium, indium, magnesium, calcium, palladium, gallanyl and vanadyl.

Suitable compounds according to the first preferred class are those conforming to the following formula:

25

octa-3,6-(RX)-Pc-M_k

III

wherein

M is a metal atom or hydrogen;

k is the inverse of half the valency of M;

30 Pc is the phthalocyanine nucleus;

X is sulphur, selenium, tellurium or NT where T is H, alkyl or aryl;

and R is a monovalent aromatic radical, preferably optionally substituted benzene or naphthalene;

or R & T together form an aliphatic or aromatic ring.

Throughout this specification the symbols, H_2Pc and MPc , in which M is a metal, e.g. Cu, Zn or Pb, will be used to indicate unmetallised and metallised phthalocyanines respectively.

5 Examples of compounds of the first preferred class and mostly conforming to Formula III are:

octa-3,6-(4-methylphenylthio)-CuPc

octa-3,6-(benzylthio)-CaPc

octa-3,6-(naphth-2-ylthio)-CuPc

10 octa-3,6-(4-methoxyphenylthio)-GePc

octa-3,6-(4-butoxyphenylthio)-CoPc

octa-3,6-(phenyltelluro)- H_2Pc

octa-3,6-(ethylthio)-NiPc

octa-3,6-(4-t-butylphenylthio)-(VO)Pc

15 octa-3,6-(hexadecylthio)-CuPc

octa-3,6-(4-methylthiophenylthio)-CuPc

octa-3,6-(4-dodecyloxyphenylthio)-CuPc

hepta-3,6-(n-octylthio)-mono-3,6-chloro-CuPc

octa-3,6-(3,4-dimethylphenylthio)- H_2Pc

20 octa-3,6-(pyrid-2-ylthio)- H_2Pc

octa-3,6-(2,4-dimethoxyphenylthio)-CuPc

phen-1,4-yleneedithio-bis[hepta-3-6-(4-thiolphenylthio)]-CuPc

hepta-3,6-(4-butylphenylthio)-mono-3,6-chloro- H_2Pc

octapiperidino-octachloro- H_2Pc

25 octa(diethylamino)- H_2Pc

octa(ethylamino)- H_2Pc

Suitable compounds from the second preferred class are those conforming to the following formulae:

30 $M_k P_c (X R)_n (Y)_m$

IV

and

$M_k P_c (X^1 - Q - X)_p (X R)_q (Y)_m$

V

wherein

M is a metal atom or hydrogen;
k is the inverse of half the valency of M;
Pc is the phthalocyanine nucleus;
X is sulphur, selenium, tellurium or NT where T is H, alkyl or
5 aryl;
R is a monovalent aromatic radical;
or R & T together form an aliphatic or aromatic ring;
n is an integer from 10 to 16;
Y is a halogen atom;
10 m is an integer from 0 to 6;
X¹ is sulphur, selenium, tellurium, oxygen or NT in which T is
H, alkyl or aryl
Q is a divalent aromatic radical;
p is an integer from 1 to 8;
15 q is an integer from 0 to 14;

provided that

(a) at least 6 of the groups represented by Q and R are
attached through linking groups X to octa-3,6 carbon atoms,
and (b) n or the sum of 2p & q is from 10 to 16, preferably
20 from 12 to 16 and more preferably 15 or 16.

Examples of compounds conforming to Formulae IV & V are:
deca(4-methylphenylthio)-pentachloro-CuPc
deca(4-t-butylphenylthio)-pentachloro-CuPc
deca(naphth-2-ylthio)-hexachloro-CuPc
25 deca(4-ethylthiophenylthio)-pentachloro-CuPc
unadeca(4-methylphenylthio)-bromo-CuPc
unadeca(4-dimethylaminophenylthio)-pentachloro-CuPc
dodeca(4-methylphenylthio)-CuPc
dodeca(4-t-butylphenylthio)-trichloro-CuPc
30 terdeca(4-butoxyphenylthio)-dichloro-InPc
pentadeca(n-butylthio)-CuPc
pentadeca(4-carboxyphenylthio)-CuPc
pentadeca(4-t-butylphenylthio)-CuPc
pentadeca(phenylseleno)CuPc

pentadeca(naphth-2-ylthio)-MgPc
pentadeca(naphth-1-ylthio)-CuPc
pentadeca(4-methoxyphenylthio)-CuPc
pentadeca(4-dodecyloxyphenylthio)-CuPc
5 pentadeca(4-methylthiophenylthio)-CuPc
pentadeca(phenylthio)-CuPc
pentadeca(4-butoxyphenylthio)-CuPc
pentadeca(n-dodecylthio)-CuPc
pentadeca(benzimidazol-2-ylthio)-CuPc
10 hexadeca(4-methylphenylthio)-CuPc
hexadeca(4-methylphenylthio)-ZnPc
hexadeca-anilino-H₂Pc
hexadeca(4-methylphenylthio)-PbPc
hexadeca(4-methylphenylthio)-H₂Pc
15 hexadeca(4-chlorophenylthio)-NiPc
hexadeca(piperidino)-H₂Pc
hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiol-phenylthio)-CuPc
hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiol-phenylthio)-H₂Pc
20 octa(phen-1,2-ylenediamino)H₂Pc
hexadeca(diethylamino)H₂Pc
hexadeca(ethylamino)H₂Pc
Preferred values for, and examples of, the groups
25 represented by R, Q and T are as given hereinbefore in respect of the organic radical. Where R and T together form an aliphatic or aromatic ring this may be, for example, pyrid-1-yl, pyrimid-1-yl, piperidin-1-yl, morpholin-1-yl, pyrrol-1-yl or pyrrolidin-1-yl.
The phthalocyanine compounds of the present invention can be
30 prepared by heating a phthalocyanine compound carrying halogen atoms attached to the peripheral carbon atoms to which it is wished attach the Group VB or Group VIB atoms with at least six equivalents of an organic thiol, or an equivalent compound in which the sulphur in the thiol group is replaced by selenium (selenol), tellurium (tellurol)
35 or NT (amine), in an organic solvent.

The compounds of the first preferred class in which X is sulphur can be prepared by heating an octa-halo-phthalocyanine, in which at least six, and more preferably all, of the halogen atoms are attached to 3,6 carbon atoms, with at least eight equivalents of an 5 organic thiol in an organic solvent,

The compounds of the second preferred class in which X is sulphur can be prepared by heating a phthalocyanine carrying at least nine halogen atoms, at least six of which are attached to 3,6 carbon atoms, with at least nine equivalents of an organic thiol in an 10 organic solvent. If the organic thiol also carries another substituent, such as a second thiol group or a hydroxy or a primary or secondary amino group, which will react with a halogen atom attached to an adjacent peripheral carbon atom on the phthalocyanine nucleus, the organic radical of the thiol may become linked to two 15 adjacent peripheral carbon atoms.

Other compounds of the preferred classes may be prepared by using, in place of the thiol, an equivalent compound in which the sulphur is replaced by selenium, tellurium or a group, NT.

The organic solvent, which need not necessarily be a liquid 20 at ambient temperatures and may only partially dissolve the reactants, preferably has a boiling point from 100°C to 300°C and more preferably from 150°C to 250°C. The organic solvent is preferably essentially inert although it may catalyse the reaction. Examples of suitable solvents are methylcyclohexanol, octanol, 25 ethylene glycol, and especially benzyl alcohol and quinoline.

Reaction is conveniently carried out under reflux, preferably from 100°C to 250°C and more preferably above 150°C, in the presence of an acid binding agent, such as potassium or sodium hydroxide or sodium carbonate, to neutralise the halo acid formed. 30 The product may be isolated by filtration or by distillation of the organic liquid. The isolated product is preferably purified by repeated recrystallisation from a suitable solvent, such as ethanol, chloroform or pyridine, and/or chromatography, using a silica-filled column and an aromatic solvent, such as toluene or xylene, as eluent.

The phthalocyanine compounds of the present invention can also be prepared by heating an o-phthalic acid derivative, especially o-phthalonitrile (o-PN), carrying substituted-thio, seleno, telluro or NT groups in the 3 & 6 positions. The process may also include 5 an unsubstituted o-PN or an o-PN carrying substituents in other than the 3 & 6 positions, provided the proportion of the o-PN carrying substituted-thio etc groups is sufficient to ensure that there are at least five substituted-thio etc, groups in the phthalocyanine product. The process is conveniently performed in a solvent in the 10 presence of a base. It may also be promoted by the addition of a catalyst, such as ammonium molybdate.

This process is analogous to the known method for preparing unsubstituted phthalocyanines from ortho-phthalic acid derivatives such as those described in Journal of the Chemical Society, (1938), 15 pp 1157-63; Advances in Inorganic Chemistry (Radiochemistry), (1965), 7, p 27 & Chemistry of Synthetic Dyes, (1971), 5, pp 241-82.

The solvent preferably has a boiling point from 50°C to 300°C, more preferably from 70°C to 200°C and need not be a liquid at ambient temperatures or completely dissolve the reactants. It is 20 preferably essentially inert though it may interact with the base, catalyse the reaction or even partially replace the substituted-thio groups in the phthalocyanine compound. Preferred solvents are aliphatic alcohols such as iso-amyl alcohol, octanol and benzyl alcohol.

25 Where an alcohol is employed as solvent it is possible for one or more alcohol residues to replace the substituted thio, etc. groups attached to the o-PN and become attached to a peripheral carbon atom of the phthalocyanine through an oxygen atoms. Such a phthalocyanine, carrying one or more organic radicals attached 30 through oxygen atoms, provided it also carries at least five organic radicals each of which is attached through a Group VB or Group VIB atom other than oxygen, is a further feature of the present invention.

The reaction is conveniently carried out between 100°C and 150°C or under reflux in the presence of a base, such as an alkoxide

formed between an alkali metal and an alcohol, preferably an aliphatic alcohol. A particularly suitable base is lithium iso-amyl oxide because lithium phthalocyanines are generally soluble in alcohols.

5 Different metals may be introduced into the phthalocyanine by heating the o-PN with a suitable salt of the appropriate metal or heating lithium phthalocyanine with a solvent soluble compound of the appropriate metal. A metal-free phthalocyanine may be obtained by acidification of the lithium phthalocyanine, in some cases by merely 10 contacting it with an acidic material, such as a silica-gel, or by heating it with a stronger acid, such as p-toluene- sulphonic acid.

15 The phthalocyanine compound in accordance with the present invention is useful for absorbing electro-magnetic energy from an infra-red source and optionally making it available as heat energy. 20 Particular applications where this property can be utilised for practical effect are infra-red inks, liquid crystal displays, infra-red protection systems, such as welding goggles, sun visors, vehicle windscreens and infra-red security systems, e.g. computer-controlled locks and alarms. The position of the absorption maximum depends upon the nature of the compound and the substrate on or in 25 which it is incorporated. Many of the compounds of the present invention exhibit a bathochromic shift of up to 50 μm when deposited on glass compared with a solution in an organic liquid.

25 A liquid crystal cell, for the formation of latent images, can be rendered laser-addressable by dissolving a compound in accordance with the present invention in the liquid crystal medium. For example,

30 Pentadeca(naphth-2-ylthio)-CuPc has an absorption maximum at 782 μm and a solubility of 0.5% in the liquid crystal material E7, which is available from BDH Chemicals, of Poole in Dorset, England, and Hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiolphenylthio)-CuPc has an absorption maximum at 820 μm and a solubility of 0.3% in the liquid crystal material, E7.

A security card can be rendered opaque to infra-red irradiation by the application to a predetermined area of an ink containing the present compound, for example, by thermal transfer or ink-jet printing. In this way a unique pattern, recognisable by a programmed detector, can be applied to the security card. By suitable choice of compound, a composite pattern absorbing at one or more wavelengths can be formed. For example,

5 Octa-3,6-(2-aminophenylthio)CuPc has an absorption maximum at 950 μm

Octa-3,6-(4-methoxyphenylthio)-CuPc has an absorption maximum at

10 805 μm and

Pentadeca-(4-methylphenylthio)-CuPc has an absorption maximum at 775 μm .

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated.

Example 1

20 A mixture of 3.06g of 4-methylphenylthiol, 1.26g of KOH and 10 ml of quinoline was stirred at 130-140°C for 60 minutes and 5.69g of octa-3,6-chloro- H_2Pc was added. The mixture was then stirred at 180°C for 1 hour and at 200-210°C for 30 minutes. The mixture was then cooled to 100°C and diluted with 50 ml of ethanol (74 OP). After cooling to 25°C the solid was filtered and dissolved in toluene. The toluene solution was passed through a silica column 25 using toluene as eluent and the main fraction collected and isolated by evaporation to yield 0.26g of dry octa-3,6-(4-methylphenylthio)- H_2Pc .

Example 2

30 A mixture of 6.29g of 4-methylphenylthiol, 3.29g of KOH and 20 ml of quinoline was stirred at 130-160°C for 90 minutes and 4.16g of octa-3,6-chloro-CuPc was added. The mixture was then stirred at 180-200°C for 5.5 hour, cooled to 80°C and diluted with 50 ml of ethanol (74 OP). After cooling to 25°C the solid was filtered, washed with ethanol and dissolved in toluene. The toluene solution

was passed through a silica column using toluene as eluent and the main fraction collected and isolated by evaporation to yield dry octa-3,6-(4-methylthio)-CuPc.

Examples 3 to 17

5 Further compounds within the scope of the present invention in accordance with Formula III were prepared by the methods of Examples 1 and 2, using equimolar quantities of appropriate thiols in place of the thiols described in the Examples, as set out in Table 1. In each product containing less than eight substituted thio groups, 10 the free 3,6-positions are occupied by chloro groups.

Table 1

<u>Ex</u>	<u>Method</u>	<u>Thiol</u>	<u>Product</u>
3	Ex 1	3-methylphenyl	octa-3,6(3-methylphenylthio)H ₂ Pc
15	4	4-t-butylphenyl	hepta-3,6(4-t-butylphenylthio)H ₂ Pc
	5	4-t-butylphenyl	octa-3,6(4-t-butylphenylthio)H ₂ Pc
	6	4-t-butylphenyl	octa-3,6(4-t-butylphenylthio)CuPc
	7	4-n-nonylphenyl	hepta-3,6(4-n-nonylphenylthio)H ₂ Pc
	8	4-dodecylphenyl	hepta-3,6(4-dodecylphenylthio)H ₂ Pc
20	9	3,4-dimethylphenyl	hexa-3,6(3,4-dimethylphenylthio)H ₂ Pc
	10	4-methoxyphenyl	octa-3,6(4-methoxyphenylthio)H ₂ Pc
	11	4-methoxyphenyl	octa-3,6(4-methoxyphenylthio)CuPc
	12	4-butoxyphenyl	octa-3,6(4-butoxyphenylthio)CuPc
	13	4-dodecyloxyphenyl	octa-3,6(4-dodecyloxyphenylthio)H ₂ Pc
25	14	4-dodecyloxyphenyl	octa-3,6(4-dodecyloxyphenylthio)CuPc
	15	naphth-2-yl	octa-3,6(naphth-2-ylthio)CuPc
	16	4-octoxyphenyl	octa-3,6(4-octoxyphenylthio)H ₂ Pc
	17	4-octoxyphenyl	penta-3,6(4-octoxyphenylthio)CuPc

30 The octa-3,6-Pcs used in Examples 1 to 17 were made from purified dichlorophthalic anhydride comprising >85% of the 3,6-dichloro isomer. The dichlorophthalic anhydride was purified by by centrifugal distillation or fractional crystallisation.

Example 18

A mixture of 12.4g of 4-methylphenylthiol, 5.6g of KOH and 20 ml of quinoline was stirred at 140°C for 60 minutes and 5.69g of tetradeccachloromonobromo-CuPc was added. The mixture was then 5 stirred vigorously at 160-180°C for 1 hour, cooled to 100°C and diluted with 50 ml of ethanol (74 OP). After cooling to ambient the solid was filtered, washed with ethanol, water and ethanol and dried to give 7.8g crude material. The crude material was passed through a silica column using toluene as eluent and the main fraction 10 collected and isolated by evaporation to yield 5.77g of dry pentadeca(4-methylthio)-CuPc.

Example 19

A mixture of 1.65g of 4-methylphenylthiol, 0.83g of KOH and 10 ml of quinoline was stirred at 140°C for 30 minutes and 2.8g of 15 tetradeccachloro-monobromo-CuPc was added. The mixture was then stirred at 180-200°C for 5 hours, cooled to 80°C and diluted with 30 ml of ethanol (74 OP). After cooling to 30°C the solid was filtered, washed with ethanol and dried to give 3.6g crude material. The crude material was passed through a silica column using toluene 20 as eluent and the main fraction collected and isolated by evaporation to yield 0.92g of dry deca(4-methylthio)-pentachloro- CuPc.

Examples 20 to 36

Further compounds within the scope of the present invention in accordance with Formula IV were prepared by the methods of 25 Examples 18 & 19, using equimolar quantities of appropriate thiols or selenols in place of the thiols described in the Examples, as set out in Table 2. In each product having less than fifteen substituted thio groups, the free positions are occupied by chloro groups.

Table 2

<u>Example</u>	<u>Thiol/Selenol</u>	<u>Product</u>
5	20 t-butylphenyl	pentadeca(t-butylphenylthio)CuPc
	21 3-methylphenyl	pentadeca(3-methylphenylthio)CuPc
	22 4-methoxyphenyl	pentadeca(4-methoxyphenylthio)CuPc
	23 4-butoxyphenyl	terdeca(4-butoxyphenylthio)CuPc
	24 4-butoxyphenyl	pentadeca(4-butoxyphenylthio)CuPc
	25 4-dodecoxyphenyl	pentadeca(4-dodecoxyphenylthio)CuPc
10	26 phenyl	pentadeca(phenylthio)CuPc
	27 2-methoxyphenyl	tetradeca(2-methoxyphenylthio)CuPc
	28 4-methylthiophenyl	pentadeca(4-methylthiophenylthio)CuPc
	29 4-ethylthiophenyl	deca(4-ethylthiophenylthio)CuPc
	30 4-chlorophenyl	pentadeca(4-chlorophenylthio)CuPc
15	31 4-(dimethylamino)phenyl	unadeca(4-dimethylaminophenylthio)CuPc
	32 naphth-1-yl	terdeca(naphth-1-ylthio)CuPc
	33 naphth-2-yl	pentadeca(naphth-2-ylthio)CuPc
	34 phenylselenol	pentadeca(phenylseleno)CuPc

20 Example 35

A mixture of 7.75g of 4-methylphenylthiol, 3.36g of KOH, and 10ml of quinoline was stirred at 130°C for 30 minutes and 3.18g of hexadecachloro-PbPc was added. The mixture was then stirred at 180-190°C for 30 minutes, cooled to 50°C and diluted with 30ml of toluene. The crude material was passed through a silica gel column using toluene as eluent and the main fraction collected. This was isolated by evaporation to give 0.45g of hexadeca(4-methylphenylthio)PbPc.

Examples 36 to 40

30 Further compounds within the scope of the present invention in accordance with Formula IV were prepared by the method of Example 35 using equimolar quantities of appropriate thiols in place of the 4-methylphenylthiol and equimolar quantities of an appropriate hexadecachloro-Pc in place of the hexadecachloro-PbPc, as set out in

Table 3. In each product having less than sixteen substituted thio groups, the free positions are occupied by chloro groups.

5

10

<u>Example</u>	<u>Thiol</u>	<u>Product</u>
36	4-methylphenyl	hexadeca(4-methylphenylthio)H ₂ Pc
37	4-methylphenyl	hexadeca(4-methylphenylthio)CuPc
38	4-methylphenyl	hexadeca(4-methylphenylthio)ZnPc
39	4-chlorophenyl	hexadeca(4-chlorophenylthio)CuPc
40	naphth-2-yl	deca(naphth-2-ylthio)H ₂ Pc

Table 3

Example 41

A mixture of 3.12g of 4-methylphen-1,2-ylenedithiol, 2.24g of KOH and 10 ml of quinoline was stirred at 30°C for 30 minutes and 2.13g of hexadecachloro-H₂Pc was added. The mixture was then stirred at 80°C for 1 hour, 100°C for 1 hour and 130°C for 1 hour. It was then cooled to 80°C and diluted with 100 ml of ethanol (74 OP). After cooling to 25°C the solid was filtered, washed twice with ethanol and dried. The crude material was passed through a silica column using chloroform as eluent. The main fraction collected, isolated by evaporation and recrystallised from toluene/ether to yield 2.00g of hepta(4-methylphen-1,2-ylenedithio)-di(4-methyl-2-thiolphenylthio)-H₂Pc.

Examples 42 & 43

Further compounds within the scope of the present invention in accordance with Formula V were prepared by the method of Example 42 using equimolar quantities of the appropriate aminothiol in place of the 4-methylphen-1,2-ylenedithiol and/or tetradecachloro-monobromo-CuPc in place of the hexadecachloro-H₂Pc, as set out in Table 4.

Table 4

	<u>Example</u>	<u>Thiol</u>	<u>Product</u>
5	42	4-methylphen-1,2-ylene dithiol	hepta(4-methylphen-1,2-dithio-ylene)-mono(4-methyl-2-thiolphenylthio)-CuPc
10	43	2-aminophenylthiol	penta(phen-1-amino-2-thio-ylene)-penta(2-aminophenylthio)-CuPc

Example 44

A mixture of 7.36g of tetra(ethylthio)-o-PN and lithium alkoxide (comprising 0.0525g of lithium in 21ml of isoamyl alcohol was stirred at 120-130°C for 2 hours and 130-135°C for a further 1 hour. After cooling to 50°C, 100ml of methanol was added and the mixture cooled to 20°C. The precipitate which formed was filtered and washed well with methanol before being dissolved in toluene. The toluene solution was passed through a silica column using toluene as eluent. The main fraction was collected and isolated by evaporation to give pentadeca(ethylthio)-monoisoamyoxy- H_2Pc .

Example 45

A mixture of 3.83g of tetra(cyclohexylthio)-o-PN and lithium alkoxide (0.023g of lithium in 7.5ml of iso-amyl alcohol) was stirred at 120-30°C for 2½ hours. After cooling to 25°C, a solution of 1.79g of zinc chloride in 25ml of anhydrous methanol was added. The mixture was then stirred at 25°C for 1 hour and at 120-30°C for 30 minutes. After cooling to 20°C, the precipitate was filtered off and washed with methanol before being dissolved in toluene. The toluene solution was passed through a silica column, using toluene as eluent and the main fraction collected. The product was isolated by evaporation to give hexadeca(cyclohexylthio)-ZnPc.

Examples 46 to 65

Further compounds within the scope of the present invention in accordance with Formula III or Formula IV were prepared by the methods of Examples 44 and 45 using equimolar quantities of

appropriate di- or tetra-(substituted-thio)-o-PN in place of the tetra(ethylthio)-o-PN of Example 44 and the tetra(cyclohexylthio)-o-PN of Examples 45 and, where appropriate, a metal chloride, as set out in Table 5.

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Table 5

	<u>Example</u>	<u>Subs-o-PN</u>	<u>Product</u>
<u>As in Example 45 (with di- or tetra-(substituted-thio)-o-PN)</u>			
	46	tetraethyl	tetradeca(ethylthio)monoamyloxy-H ₂ Pc
	47	tetraethyl	(ethylthio) _{15.3} (amyloxy) _{0.7} -H ₂ Pc
10	48	tetra-n-propyl	hexadeca(n-propylthio)-H ₂ Pc
	49	tetra-i-propyl	pentadeca(i-propylthio)monoamyloxy-H ₂ Pc
	50	tetra-n-butyl	pentadeca(n-butylthio)monoamyloxy-H ₂ Pc
	51	tetra-n-pentyl	pentadeca(n-pentylthio)monoamyloxy-H ₂ Pc
	52	tetraethyl/tetrabutyl	octa(butylthio)octa(ethylthio)-H ₂ Pc
15	53	tetra(ethyl/butyl) (random)	octa(butylthio)octa(ethylthio)-H ₂ Pc
	54	tetracyclohexyl	pentadeca(cyclohexylthio)monoamyloxy-H ₂ Pc
	55	tetra-n-octyl	hexadeca(n-octylthio)-H ₂ Pc
	56	tetra-s-butyl	pentadeca(s-butylthio)monoamyloxy-H ₂ Pc
20	57	tetrabenzyl	pentadeca(benzylthio)monoamyloxy-H ₂ Pc
	58	tetraphenyl	hexadeca(phenylthio)-H ₂ Pc
	59	3,6-di(iso-propyl)	octa-3,6-(isopropylthio)-H ₂ Pc
<u>As in Example 46 (with tetra(substituted-thio)-o-PN & CuCl₂)</u>			
	60	tetra-n-propyl	pentadeca(n-propylthio)monoamyloxy-CuPc
25	61	tetra-n-pentyl	pentadeca(n-pentylthio)monoamyloxy-CuPc
	62	tetracyclohexyl	pentadeca(cyclohexylthio)monoamyloxy-CuPc
	63	tetra-s-butyl	pentadeca(s-butylthio)monoamyloxy-CuPc
	64	tetrabenzyl	pentadeca(benzylthio)monoamyloxy-CuPc
<u>As in Example 46 (with tetra(substituted-thio)-o-PN & PbCl₂)</u>			
30	65	tetracyclohexyl	pentadeca(cyclohexylthio)monoamyloxy-PbPc

Example 66

A mixture of 0.46g of dipiperidino-dichloro-o-PN and lithium alkoxide (comprising 0.007g of lithium and 5ml of isoamyl alcohol) was stirred at 120-130°C for 20 minutes. After cooling to 20°C, 5 10ml of chloroform was added and the mixture passed through a silica column using chloroform as eluent. A fraction was collected and isolated by evaporation to give octapiperidino-octachloro-H₂Pc.

The dipiperidino-dichloro-o-PN was prepared by reacting piperidine with tetra-chloro-o-PN in dimethylformamide and potassium 10 carbonate using the method described in UK 1,489,394.

In all the above preparations structures were confirmed by elemental analysis and the products were characterised by the determination of melting points, absorption maxima and/or extinction 15 coefficients.

Properties of Infra-red Absorbers

The products of the Examples have the properties set out in Table 6. Absorption maxima were measured as solutions in chloroform 20 (Chlor), toluene (Tol) or after deposition on glass (Glass) unless otherwise indicated. Extinction coefficients were determined in toluene or the only solvent in which the absorption maximum was recorded.

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Table 6

	<u>Example</u>	<u>Absorption Maxima (mμm)</u>			<u>Extinction Coefficient</u>	<u>Melting Point (°C)</u>
		<u>Chlor</u>	<u>Tol</u>	<u>Glass</u>		
5	1	813	805	828	170,000	>200
	2	797	787	797	156,000	>200
	3	805	797	818	160,000	>250
	4	798	790		173,000	>250
10	5	793		797	152,000	>250
	6	803		797	216,000	>280
	7	800		809		75
	8	789	787	795		70
	9	807	803	830		>200
15	10	799	792		161,500	
	11	805		813	155,000	
	12	800	786			95
	13	818	808	859		<70
20	14	807	794	822		
	15	799		796	136,000	
	16	816	806	846		75
	17	775				
25	18	775	768	790	169,000	120
	19	758	752	770	174,000	148
	20	774	760	784	142,000	128
	21	771	766	786		95
	22	786		801	190,000	
	23	775	768	797	158,000	140
	24	786	780	801	182,000	100

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Table 6 (cont'd)

<u>Example</u>	<u>Absorption Maxima (μμm)</u>			<u>Extinction Coefficient</u>	<u>Melting Point (°C)</u>
	<u>Chlor</u>	<u>Tol</u>	<u>Glass</u>		
5	25	778	770	792	120
	26	772	768	794	
	27	770			
10	28	788	784	810	168
	29	756	752		
	30	774		787	
	31	782		805	
	32	765	760		
15	33	786	781	799	143
	34	776			
	35	769		792	
	36	769			
	37	778	770	796	
20	38	768		791	160
	39	770		789	
	40	744			
	41	800	797	832	
	42	790	787	828	
25	43	909 (in pyridine)			223
	44	804	807	827	
	45	846	852	860	
	46	801	802		
	47	805	808	830	
30	48	802	800	819	142
	49	809		823	
	50	807		817	
	51	802	802		
	52	809	805	815	
	53	803	797	815	>200
	54	812	810	818	

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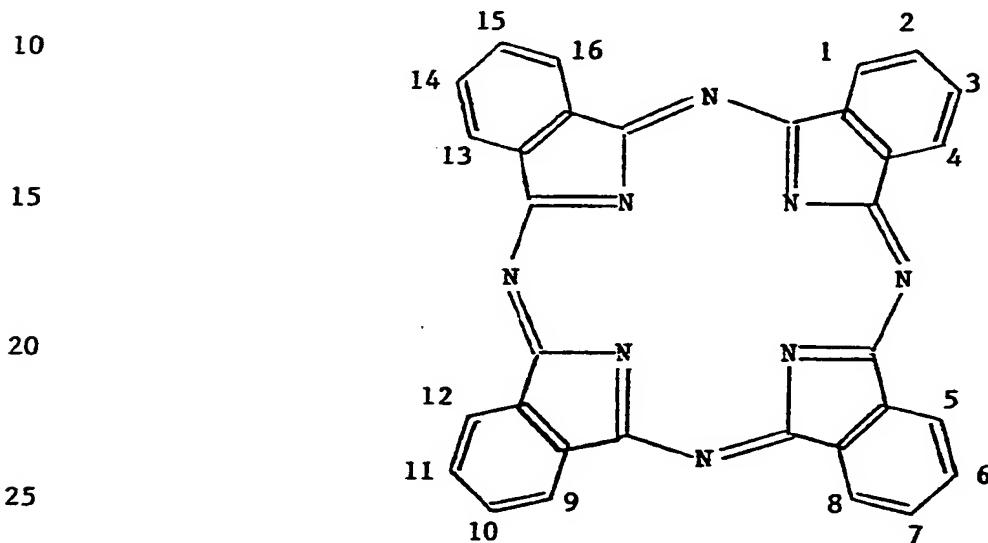
Dn. 33051

Table 6 (cont'd)

<u>Example</u>	<u>Absorption Maxima (μμm)</u>			<u>Extinction Coefficient</u>	<u>Melting Point (°C)</u>
	<u>Chlor</u>	<u>Tol</u>	<u>Glass</u>		
5	55	818	811		<30
	56	805	801	133,000	260-280
	57	810	809	84,000	100-180
10	58	790			
	59	802		167,000	
	60	783	785	170,500	260
	61	784	783	182,000	<30
	62	789	781	163,000	286
	63	787	778	168,000	270-280
	64	797	789	109,000	100-200
	65	838	830	111,000	175-230
	15	66	835		

CLAIMS

1. A phthalocyanine compound in which each of five of the peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 and 16 positions of the phthalocyanine nucleus, as shown in Formula I, is linked by an
5 atom from Group VB or Group VIB of the Periodic Table, other than oxygen, to a carbon atom of an organic radical.



2. A phthalocyanine compound according to Claim 1 wherein each
30 of the eight peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 and 16 positions of the phthalocyanine nucleus is linked by an atom from Group VB or Group VIB of the Periodic Table, other than oxygen, to a carbon atom of an organic radical.

3. A phthalocyanine compound according to Claim 2 wherein the
35 remaining peripheral carbon atoms of the phthalocyanine nucleus are unsubstituted.

4. A phthalocyanine compound according to Claim 1 or Claim 2 wherein each of from one to eight of the remaining peripheral carbon atoms of the phthalocyanine nucleus is linked by an atom from
40 Group VB or Group VIB of the Periodic Table to a carbon atom of an organic radical.

5. A phthalocyanine compound according to any one of Claims 1, 2 and 4 wherein each of fifteen or sixteen of the peripheral carbon atoms of the phthalocyanine nucleus is linked by an atom from Group VB or Group VIB of the Periodic Table to a carbon atom of an organic radical.
6. A phthalocyanine compound according to any one of Claims 1 to 5 having an absorption maximum above 750 mμm.
7. A phthalocyanine compound according to any one of Claims 1 to 6 wherein the organic radical is an optionally substituted 10 aliphatic, cycloaliphatic or aromatic radical.
8. A phthalocyanine compound according to Claim 7 wherein the organic radical is an optionally substituted phenyl, naphthyl or mono- or bi-cyclic heteroaromatic radical.
9. A phthalocyanine compound according to any one of Claims 1 to 8 wherein the organic radical is bivalent and attached to adjacent peripheral carbon atoms on the phthalocyanine nucleus through atoms from Group VB or Group VIB of the Periodic Table.
10. A phthalocyanine compound according to any one of Claims 1 to 9 wherein the atom from Group VB or Group VIB of the Periodic Table is sulphur, selenium, tellurium or nitrogen.
11. A phthalocyanine compound according to any one of Claims 4 to 10 wherein at least one of the peripheral carbon atoms of the phthalocyanine nucleus is linked to an organic radical through an oxygen atom.
12. A process for the preparation of a phthalocyanine compound according to Claim 3 in which the atom from Group VIB is sulphur which comprises heating an octa-3,6-halo-phthalocyanine with at least eight equivalents of an organic thiol in an organic solvent.
13. A process for the preparation of a phthalocyanine compound according to Claim 3 in which the atom from Group VIB is sulphur which comprises heating a 3,6-di(substituted-thio)phthalonitrile in a solvent in the presence of a base.
14. A process for the preparation of a phthalocyanine compound according to Claim 4 in which the atom from Group VIB is sulphur

which comprises heating a phthalocyanine carrying from nine to sixteen halo groups attached to the preripheral carbon atoms with from nine to sixteen equivalents of an organic thiol in an organic solvent.

5 15. A substrate capable of absorbing infra-red radiation containing or coated with a phthalocyanine compound according to any one of Claims 1 to 11.



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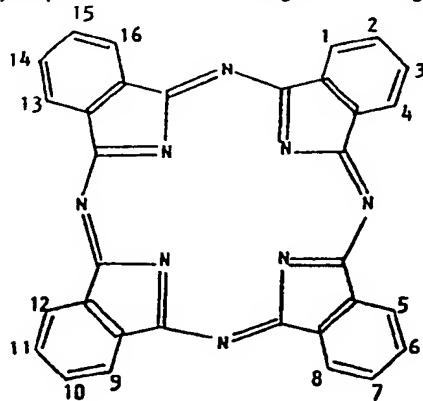
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⑷ Infra-red absorber.

⑷ A infra-red absorbing phthalocyanine compound in which each of at least five of the peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 or 16 positions (the "3,6-positions") of the phthalocyanine nucleus, as shown in Formula I, is linked by an atom from Group VB or Group VIB of the Periodic Table, other than oxygen, to a carbon atom of an organic radical. In preferred compounds each of the eight 3,6-positions is linked by an atoms from Group VB or Group VIB, especially sulphur, selenium or nitrogen, to an organic radical.



EP 0 155 780 A3



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EUROPEAN SEARCH REPORT

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EP 85 30 1291

DOCUMENTS CONSIDERED TO BE RELEVANT						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)			
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A		1-4, 7, 10	<p>TECHNICAL FIELDS SEARCHED (Int. Cl.4)</p> <p>C 07 D 487/00 C 09 B 47/00</p>			
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search BERLIN</td> <td>Date of completion of the search 06-08-1985</td> <td>Examiner HASS C V F</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search BERLIN	Date of completion of the search 06-08-1985	Examiner HASS C V F
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Application number

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Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
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A	DE-A-2 455 675 (CIBA-GEIGY AG) * Claims 1-3, 6-11 *	1, 7, 8, 10, 13	
A	DE-A-2 531 823 (PRODUITS CHIMIQUES UGINE KUHLMANN) * Claim 1; examples 3, 5, 6 *	1, 7, 10, 12	
D, A	CHEMISTRY OF SYNTHETIC DYES, vol. 5, 1971; G. BOOTH "Phthalocyanines", pages 241-282 * Page 244, line 8 - page 245, line 7; page 267, paragraph "Thiocethers" *	1, 2, 13	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
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The present search report has been drawn up for all claims			
Place of search BERLIN	Date of completion of the search 06-08-1985	Examiner HASS C V E	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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A : technological background	O : non-written disclosure		
P : intermediate document			



DOCUMENTS CONSIDERED TO BE RELEVANT			Page 3
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A	--- DE-A-2 439 600 (HOECHST AG) * Examples 1, 3 *	12	
A	--- DE-A-2 637 861 (ICI LTD.) * Example 1 *	14	
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The present search report has been drawn up for all claims

Place of search BERLIN	Date of completion of the search 06-08-1985	Examiner HASS C V F
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